

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

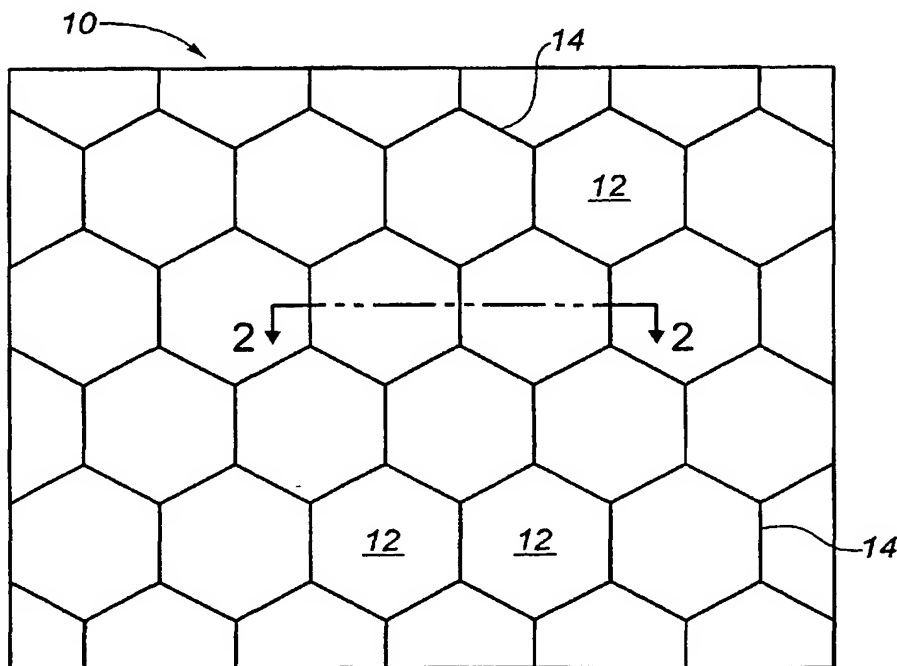
PCT

(10) International Publication Number
WO 02/19445 A2

- (51) International Patent Classification⁷: **H01M 4/00**
- (21) International Application Number: **PCT/CA01/01235**
- (22) International Filing Date: **30 August 2001 (30.08.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
60/229,322 **1 September 2000 (01.09.2000)** **US**
- (71) Applicant: **GLOBAL THERMOELECTRIC INC.**
[CA/CA]; 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA).
- (72) Inventors: **TANG, Zheng**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA). **GHOSH, Debabrata**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA). **PREDIGER, Dennis**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA). **MARTELL, Frank**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA).
- (74) Agent: **BENNETT JONES LLP**; 1000 ATCO Centre, 10035 - 105 Street, Edmonton, Alberta T5J 3T2 (CA).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report

[Continued on next page]

(54) Title: **ELECTRODE PATTERN FOR SOLID STATE IONIC DEVICES**



(57) Abstract: A solid oxide fuel cell electrode is stable during thermal cycling and includes a plurality of discrete geometric elements tightly packed on the electrolyte surface. Preferably, the geometric elements are regular hexagons, creating a "honeycomb" pattern electrode.

WO 02/19445 A2



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ELECTRODE PATTERN FOR SOLID STATE IONIC DEVICES

5

Field of the invention:

10 The present invention relates to macroscopic patterns applied to electrodes of solid state ionic devices.

Background of the invention:

15 Solid oxide fuel cells ("SOFC's") are high temperature electrochemical devices fabricated primarily from ceramic oxides. Typically they contain an oxygen ion conducting solid electrolyte, such as stabilized zirconia. The electrolyte is usually a thin dense film that separates two porous electrodes, an anode and a cathode. An interconnection is usually employed which is stable in both oxidizing and reducing environments, and provides a manifold to conduct fuel and an oxidant, usually air, separately into the cell. The cell operates by electrochemically oxidizing a gaseous fuel, such as hydrogen, to produce electricity and heat. The electrode must be compatible with the chemical, electrical, and mechanical properties such as thermal expansion rates of the solid electrolyte to which it is attached.

25 The use of cermet electrodes for SOFC's is well known in the art. The cermet electrode is manufactured by applying a mixture of a metallic element, an oxide, or simply yttria stabilized zirconia onto the electrolyte of a cell. Various methods are known to apply the green state cermet electrode on a solid electrolyte. Examples of such prior art methods include dipping, spraying, screen printing, and vapour deposition. In order to maximize the electrochemical active area, an electrode is applied to the entire electrolyte

30

surface. Finally, a sintering process is usually applied to bond the cermet electrode to the electrolyte. The microstructure of a sintered cermet electrode is more amenable to modification and control, allowing the performance of the cell to be optimized.

5 Despite the advantages of a cermet electrode described in the prior art, the bond between a cermet electrode and the electrolyte is usually a weak one. This arises from the difference in the coefficient of thermal expansion between the cermet electrode and the electrolyte. Also the bonding between a metallic element and an oxide electrolyte relies on weak physical bonding rather than strong chemical bonding. Thus the
10 detachment of a cermet electrode from the electrolyte is a common problem, which occurs both during SOFC manufacturing and testing. This reduces the active area for the electrode reaction, and increases the overpotential lost at the interface. This problem increases in severity as the size of the SOFC increases.

15 Thermal cycling capability is very important for a number of commercial applications of SOFC's. However, thermal cycling magnifies the stresses between the electrode and the electrolyte because of the difference in thermal expansion coefficients and rates. In order to suppress the problem, one solution is to increase the oxide component to enhance the bonding as well as to match the thermal expansion coefficient
20 to an allowable value. However, this improvement is based upon sacrificing the electrical conductivity of the cermet electrode because of the reduction of the metallic component. According to the percolation theory, when the volume of the electronic conducting phase decreases toward 30 percent, the conductivity will quickly decrease. As a result, the power density of the SOFC will decrease due to the increasing electrical resistance inside
25 the cermet electrode. To a certain extent the problems with the prior art as described herein apply to other types of electrodes in addition to cermet electrodes, such as for example, metal oxides and LSM electrodes, since there is usually a difference in thermal expansion coefficients.

30 Thus the optimization of the cermet electrode through composition adjustments is limited. Prior art attempts to solve the thermal expansion problems have used skeletal

embedded growth of primarily ionically conducting yttria stabilized zirconia. The skeletal growth extends from the electrolyte/electrode interface into a porous metallic layer, with the composite structure comprising the porous cermet electrode. In one example, bonding of the porous nickel anode to the solid oxide electrolyte was accomplished with a modified electrochemical vapour deposition (EVD) process. This process provides well bonded anodes having good mechanical strength and thermal expansion characteristics, however overall cell performance is lower than with other bonding methods. The EVD process, while producing acceptable quality electrodes, is labour intensive and very expensive. A simpler and less expensive method of producing electrodes which mitigate the difficulties of the prior art is needed, without sacrificing electrode performance.

Summary of the invention

The present invention relates to electrodes which are applied to the electrolyte in a pattern. The pattern physically breaks a large monolithic electrode into a plurality of small discrete elements. Thus the stress caused by the thermal expansion mismatch will be limited to a much smaller area, with a corresponding reduction in strain at the interface of the small elements, thereby reducing delamination and increasing thermal cycling capability.

In accordance with a broad aspect of the invention, the electrode is divided into many small discrete areas or elements, rather than a monolithic electrode. The gaps between the elements are preferably kept as narrow or small as possible to minimize the loss of active area. In a preferred embodiment, the elements are hexagonal in shape, creating a honeycomb array of electrode elements.

In accordance with another broad aspect of the invention, the patterned layer is sintered after being deposited upon the substrate.

Brief description of the drawing:

Figure 1 shows a schematic of the electrode pattern of one embodiment of a solid oxide fuel cell of the present invention.

Figure 2 is a cross-sectional view of a electrolyte and electrode layers of fuel cell of Figure 1.

Detailed description of the invention:

In Figure 1, a pattern as applied to an electrode is illustrated. The present invention is applicable to cathodes or anodes. The surface of the electrode (10) is divided into uniformly sized elements (12), which are separated by gaps (14). The elements (12) are hexagonal and arranged into closely packed "honeycomb" array. A hexagonal shape is preferred as this permits the maximum number of elements to be packed into a two dimensional plane, while allowing the internal corner angles of each element to be relatively large. In the specific example of a hexagonal element, the interior angle is 120 degrees. A large corner angle is important to reduce the stress concentrations at the corners of the elements, and thus reduce the probability of cracking and peeling. Thus, a hexagon with a corner angle of 120 degrees will be more stable than a square having a corner angle of 90 degrees or a triangle having a corner angle of 60 degrees. However, the present invention is not intended to exclude variations comprising pentagonal, quadrilateral, triangular or other geometric shapes.

The polygonal shapes of the present invention may or may not be regular polygons but should preferably be symmetrical. A regular polygon is one where all of the internal angles are the same and the length of each side of the polygon are equal. As will be apparent, a tightly packed array of elements may be achieved with symmetrical but not regular polygons.

The hexagonal pattern is also more forgiving of slight mismatches between the elements than other geometric patterns, such as squares, caused by movement during sintering and thermal cycling of the cell, while maintaining the maximum active area of electrode. The hexagonal pattern allows for the area lost to the inter element gaps (14) to be minimized in the case of element mismatch. The hexagonal pattern also allows the gaps (14) between the elements (12) to be kept to a minimum. It is preferred that the shapes be interlocking or complementary so that the gaps (14) are minimized. Preferably, the surface area lost to the gaps is less than about 5%, more preferably less than about 2%. In the embodiment illustrated in Figure 1, less than 1% of the electrode surface area is taken by the gaps (14) between the elements (12). Although hexagons are the preferred shape of the current embodiment, any shape may be used, such as pentagons, squares and triangles, although not all shapes may have the same advantages of hexagons as described herein.

In the example shown, the planar electrode is about 90mm square while each hexagonal element is about 8.6 mm wide, resulting in a 10 x 10 array of hexagonal elements. The gaps (14) are less than about 0.15 mm wide. The border of the electrode may be a contiguous border element or may comprise a plurality of whole or partial hexagonal elements.

In one embodiment, the array of discrete elements may be screen printed onto the electrolyte. A screen with a pattern such as the pattern shown in Figure 1 may be made using conventional screen fabrication techniques as used in the thick film screen printing industry. If the desired electrode is a cathode, a cermet cathode paste may be screen printed on the electrolyte through the patterned screen. After drying, it is further sintered at about 1300 °C. A contact paste of lanthanum cobaltate (LaCoO_3) is then screen printed on top of the cathode before loading the cell into a fuel cell stack. This layer is interposed between the electrodes and an interconnect to improve electrical conductivity and mechanical bonding characteristics between them. This layer has the additional effect of physically separating the layers and preventing interdiffusion among chemically

incompatible components during testing. The contact paste layer is not essential but is preferred. If the desired electrode is an anode, the contact paste layer is not necessary.

As will be apparent to those skilled in the art, various modifications, adaptations
5 and variations of the foregoing specific disclosure can be made without departing from
the scope of the invention claimed herein.

Claims:

1. A solid oxide fuel cell comprising an electrode layer applied to an electrolyte layer wherein the electrode layer is not contiguous but rather is formed from a plurality of substantially discrete elements separated by substantially uniform gaps.
2. The solid oxide fuel cell of claim 1 wherein the discrete elements are polygonal in shape.
3. The solid oxide fuel cell of claim 2 wherein the polygonal discrete elements are hexagonal in shape.
4. The solid oxide fuel cell of claim 3 wherein said hexagons are regular hexagons.
5. The solid oxide fuel cell of claim 1 further comprising a contact paste layer applied to the electrode layer.
6. The solid oxide fuel cell of claim 5 wherein the contact paste layer is lanthanum cobaltate.
7. The solid oxide fuel cell of claim 6 wherein the contact paste layer is not sintered prior to use.
8. The solid oxide fuel cell of claim 1 wherein the gaps take up less than about 5% of the surface area of the electrode.
9. The solid oxide fuel cell of claim 8 wherein the gaps take up less than about 2% of the surface area of the electrode.

10. The solid oxide fuel cell of claim 9 wherein the gaps take up less than about 1% of the surface area of the electrode.

5 11. A solid oxide fuel cell comprising an electrode layer applied to an electrolyte layer wherein the electrode layer is not contiguous but rather is formed from a plurality of substantially discrete hexagonal elements separated by substantially uniform gaps, wherein the gaps take up less than about 2% of the surface area of the electrode.

10 12. A method of applying an electrode layer to an electrolyte layer in a SOFC comprising the steps of:

(a) providing a screen defining a pattern comprising a plurality of discrete elements;

15 (b) screen printing an electrode paste through the screen and onto the electrolyte such that the resulting electrode layer comprises a plurality of discrete elements which are separated by substantially uniform and narrow gaps;

(c) sintering the electrode layer.

20

13. The method of claim 12 further comprising the step of adding a contact paste layer over the electrode layer.

25 14. The method of claim 12 wherein the discrete elements have a regular hexagonal shape and the pattern comprises a honeycomb array of elements.

1/1

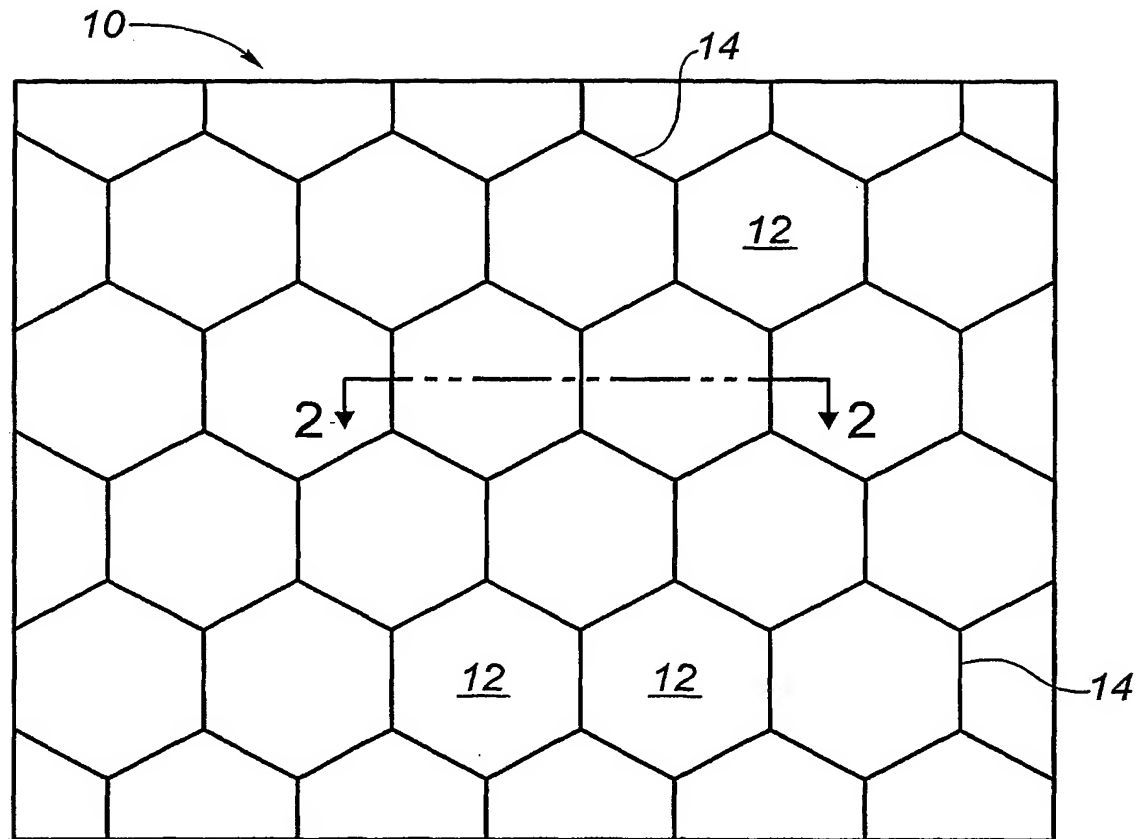


FIG. 1

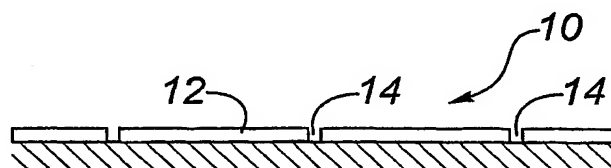


FIG. 2

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 March 2002 (07.03.2002)

PCT

(10) International Publication Number
WO 02/019445 A3

(51) International Patent Classification⁷: **H01M 8/12**

(21) International Application Number: PCT/CA01/01235

(22) International Filing Date: 30 August 2001 (30.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/229,322 1 September 2000 (01.09.2000) US

(71) Applicant: **GLOBAL THERMOELECTRIC INC.**
[CA/CA]; 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA).

(72) Inventors: **TANG, Zheng**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA). **GHOSH, Debabrata**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA). **PREDIGER, Dennis**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA). **MARTELL, Frank**; c/o 4908 - 52 Street S.E., Calgary, Alberta T2B 3R2 (CA).

(74) Agent: **BENNETT JONES LLP**; 1000 ATCO Centre, 10035 - 105 Street, Edmonton, Alberta T5J 3T2 (CA).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

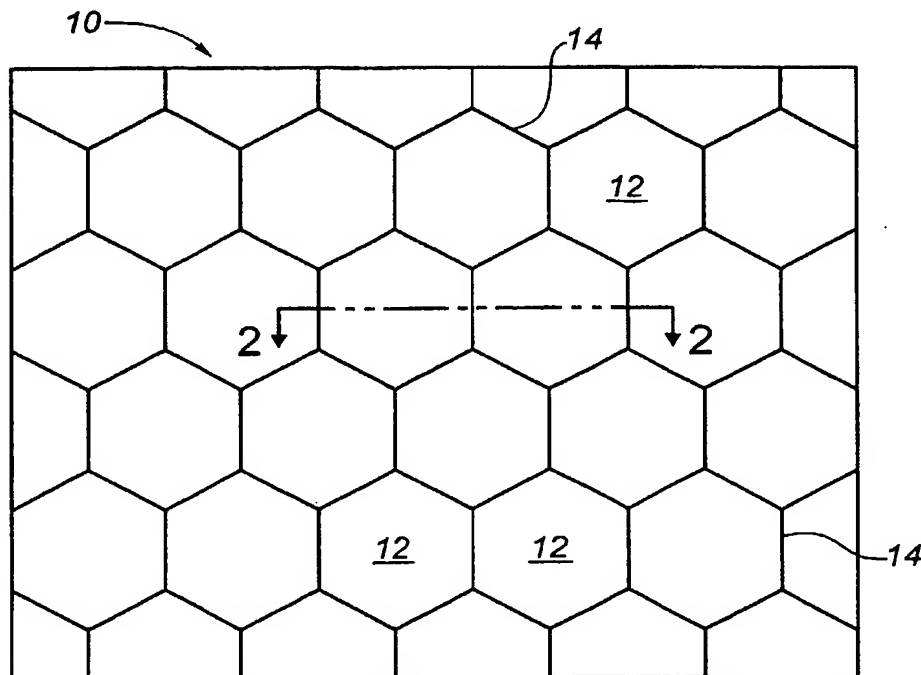
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

[Continued on next page]

(54) Title: ELECTRODE PATTERN FOR SOLID OXIDE FUEL CELLS



(57) Abstract: A solid oxide fuel cell electrode is stable during thermal cycling and includes a plurality of discrete geometric elements (12) tightly packed on the electrolyte surface. Preferably, the geometric elements are regular hexagons, creating a "honeycomb" pattern electrode.



WO 02/019445 A3



— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(88) Date of publication of the international search report:

16 January 2003

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 01/01235

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M8/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No. -
X	US 3 402 230 A (WHITE JR DONALD W) 17 September 1968 (1968-09-17) column 2, line 25 - line 57 claims 1-5	1,8,9, 11,12
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 273 (E-0940), 13 June 1990 (1990-06-13) -& JP 02 087471 A (NKK CORP), 28 March 1990 (1990-03-28) abstract	1,8,9, 11,12
X	EP 0 834 949 A (NGK INSULATORS LTD) 8 April 1998 (1998-04-08) page 7, line 53 -page 8, line 1 page 11, line 6 - line 9 page 11, line 22 - line 29	1-4,8,9, 11,12,14

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

11 November 2002

Date of mailing of the international search report

15/11/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Gamez, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 01/01235

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	D. GHOSH AND AL: "Performance of anode supported planar SOFC cells" ELECTROCHEMICAL SOCIETY PROCEEDINGS, vol. 99, no. 19, 1999, pages 822-829, XP008010165 page 823, paragraph 5 -page 824, paragraph 1; figure 1 page 825, paragraph 1 page-825 -	1,5-7, 12,13
P,A	----- EP 1 113 518 A (CORNING INC) 4 July 2001 (2001-07-04) column 2, line 44 - line 56 column 3, line 33 -column 4, line 7 -----	1,12

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 01/01235

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3402230	A	17-09-1968	DE 1596119 A1 FR 1479887 A GB 1148581 A	01-04-1971 05-05-1967 16-04-1969
JP 02087471	A	28-03-1990	NONE	
EP 0834949	A	08-04-1998	JP 10199549 A JP 3126939 B2 JP 10151702 A EP 0834949 A2 JP 2001155743 A US 6183609 B1 US 5964991 A	31-07-1998 22-01-2001 09-06-1998 08-04-1998 08-06-2001 06-02-2001 12-10-1999
EP 1113518	A	04-07-2001	EP 1113518 A1 JP 2001229935 A US 2002076593 A1	04-07-2001 24-08-2001 20-06-2002

THIS PAGE BLANK (USPTO)